

22 JAN 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
REQUEST FOR FILING NATIONAL PHASE OF  
PCT APPLICATION UNDER 35 U.S.C. 371 AND 37 CFR 1.494 OR 1.495

To: Hon. Commissioner of Patents  
Washington, D.C. 20231



00909

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELECTED OFFICE (DO/EO/US)

Atty Dkt: PM 276595 /DPW/EM/U187  
M# /Client Ref.

From: Pillsbury Madison & Sutro LLP, IP Group:

Date: January 22, 2001

This is a **REQUEST** for **FILING** a PCT/USA National Phase Application based on:

1. International Application <u>PCT/GB99/02206</u> <u>1</u> country code	2. International Filing Date <u>9 July 1999</u> Day MONTH Year	3. Earliest Priority Date Claimed <u>21 July 1998</u> Day MONTH Year (use item 2 if no earlier priority)
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4. Measured from the earliest priority date in item 3, this PCT/USA National Phase Application Request is being filed within:

(a) ☐ 20 months from above item 3 date (b) ☒ 30 months from above item 3 date,

(c) Therefore, the due date (unextendable) is January 21, 2001

5. Title of Invention ACRYLIC POLYMER COMPOSITION

6. Inventor(s) ROBERTSON et al.

Applicant herewith submits the following under 35 U.S.C. 371 to effect filing:

7. ☒ Please immediately start national examination procedures (35 U.S.C. 371 (f)).

8. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2)) is transmitted herewith (file if in English but, if in foreign language, file only if not transmitted to PTO by the International Bureau) including:

- a. ☐ Request;  
b. ☒ Abstract;  
c. 9 pgs. Spec. and Claims;  
d.        sheet(s) Drawing which are ☐ informal ☐ formal of size ☐ A4 ☐ 11"

9. ☒ A copy of the International Application has been transmitted by the International Bureau.

10. A translation of the International Application into English (35 U.S.C. 371(c)(2))

- a. ☐ is transmitted herewith including: (1) ☐ Request; (2) ☐ Abstract;  
(3)        pgs. Spec. and Claims;  
(4)        sheet(s) Drawing which are:  
☐ informal ☐ formal of size ☐ A4 ☐ 11"
- b. ☒ is not required, as the application was filed in English.  
c. ☐ is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.  
d. ☐ Translation verification attached (not required now).

11. ☒ **PLEASE AMEND** the specification before its first line by inserting as a separate paragraph:

- a. ☒ --This application is the national phase of international application PCT/GB99/02206  
filed July 9, 1999 which designated the U.S. and that international  
application ☒ was ☐ was not published under PCT Article 21(2) in English.--  
b. ☐ --This application also claims the benefit of U.S. Provisional Application No.  
60/       , filed        .--

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12. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., **before 18th month** from first priority date above in item 3, are transmitted herewith (file only if in English) including:
13. ☒ PCT Article 19 claim amendments (if any) have been transmitted by the International Bureau
14. ☐ Translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., of **claim amendments** made before 18th month, is attached (**required by 20th month from the date in item 3 if box 4(a) above is X'd, or 30th month if box 4(b) is X'd, or else amendments will be considered canceled**).
15. **A declaration of the inventor** (35 U.S.C. 371(c)(4))
- a. ☒ is submitted herewith ☐ Original ☒ Facsimile/Copy
- b. ☐ is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.

16. **An International Search Report (ISR):**

- a. Was prepared by ☒ European Patent Office ☐ Japanese Patent Office ☐ Other
- b. ☒ has been transmitted by the international Bureau to PTO.
- c. ☒ copy herewith (2 pg(s).) ☒ plus Annex of family members (1 pg(s).).

17. **International Preliminary Examination Report (IPER):**

- a. ☒ has been transmitted (if this letter is filed after 28 months from date in item 3) in English by the International Bureau with Annexes (if any) in original language.
- b. ☐ copy herewith in English.
- c.1 ☒ IPER Annex(es) in original language ("Annexes" are amendments made to claims/spec/drawings during Examination) including attached amended:
- c.2 ☒ Specification/claim pages # \_\_\_\_\_ claims #2  
Dwg Sheets # \_\_\_\_\_
- d. ☐ Translation of Annex(es) to IPER (**required by 30<sup>th</sup> month due date, or else annexed amendments will be considered canceled**).

18. **Information Disclosure Statement** including:

- a. ☒ Attached Form PTO-1449 listing documents
- b. ☒ Attached copies of documents listed on Form PTO-1449
- c. ☒ A concise explanation of relevance of ISR references is given in the ISR.

19. ☒ **Assignment** document and Cover Sheet for recording are attached. Please mail the recorded assignment document back to the person whose signature, name and address appear at the end of this letter.

20. ☐ Copy of Power to IA agent.

21. ☐ **Drawings** (complete only if 8d or 10a(4) not completed): \_\_\_\_\_ sheet(s) per set: ☐ 1 set informal;  
☐ Formal of size ☐ A4 ☐ 11"

22. Small Entity Status ☐ is **Not** claimed ☐ is claimed (**pre-filing confirmation required**)

22(a) \_\_\_\_\_ (No.) Small Entity Statement(s) enclosed (since 9/8/00 Small Entity Statements(s) not essential to make claim)

23. **Priority** is hereby claimed under 35 U.S.C. 119/365 based on the priority claim and the certified copy, both filed in the International Application during the international stage based on the filing in (country) GREAT BRITAIN of:

	<u>Application No.</u>	<u>Filing Date</u>		<u>Application No.</u>	<u>Filing Date</u>
(1)	98 15730.8	July 21, 1998	(2)	_____	_____
(3)	_____	_____	(4)	_____	_____
(5)	_____	_____	(6)	_____	_____

- a. ☒ See Form PCT/IB/304 sent to US/DO with copy of priority documents. If copy has not been received, **please proceed promptly to obtain same from the IB**.
- b. ☐ Copy of Form PCT/IB/304 attached.

RE: USA National Filing of P B99/02206

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24. Attached: See Preliminary Amendment

25. Preliminary Amendment:

25.5 Per Item 17.c2, **cancel original** pages #\_\_\_\_\_, claims #\_\_\_\_\_, Drawing Sheets #26. **Calculation of the U.S. National Fee (35 U.S.C. 371 (c)(1)) and other fees is as follows:**Based on amended claim(s) per above item(s) ☐ 12, ☐ 14, ☐ 17, ☐ 25, ☐ 25.5 (hilite)

Total Effective Claims	10	minus 20 =	0	x \$18/\$9	=	\$0	966/967
Independent Claims	3	minus 3 =	0	x \$80/\$40	=	\$0	964/965
If any proper (ignore improper) Multiple Dependent claim is present,				add\$270/\$135	+	0	968/969

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(4)): →→ **BASIC FEE REQUIRED, NOW** →→→→A. If country code letters in item 1 are **not** "US", "BR", "BB", "TT", "MX", "IL", "NZ", "IN" or "ZA"

See item 16 re:

1. Search Report was <u>not</u> prepared by EPO or JPO	-----	add\$1000/\$500		960/961
2. Search Report was prepared by EPO or JPO	-----	add\$860/\$430	+860	970/971

**SKIP B, C, D AND E UNLESS country code letters in item 1 are "US", "BR", "BB", "TT", "MX", "IL", "NZ", "IN" or "ZA"**

→ <input type="checkbox"/> B.	If USPTO did not issue <u>both</u> International Search Report (ISR) <u>and</u> (if box 4(b) above is X'd) the International Examination Report (IPER),	-----	add\$970/\$485	+0	960/961
→ <input type="checkbox"/> C.	If USPTO issued ISR but not IPER (or box 4(a) above is X'd),	-----	add\$710/\$355	+0	958/959
→ <input type="checkbox"/> D.	If USPTO issued IPER but IPER Sec. V boxes <u>not all</u> 3 YES,	-----	add\$690/\$345	+0	956/957
→ <input type="checkbox"/> E.	If international preliminary examination fee was paid to USPTO <u>and</u> Rules 492(a)(4) and 496(b) <u>satisfied</u> (IPER Sec. V <u>all</u> 3 boxes YES for <u>all</u> claims),	-----	add \$100/\$50	+0	962/963

27. **SUBTOTAL =** \$86028. If Assignment box 19 above is X'd, add Assignment Recording fee of ---\$40 +40 (581)29. Attached is a check to cover the ----- **TOTAL FEES** \$900

Our Deposit Account No. 03-3975

Our Order No. 81903 276595  
C# M#

00909

**CHARGE STATEMENT:** The Commissioner is hereby authorized to charge any fee specifically authorized hereafter, or any missing or insufficient fee(s) filed, or asserted to be filed, or which should have been filed herewith or concerning any paper filed hereafter, and which may be required under Rules 16-18 and 492 (missing or insufficient fee only) now or hereafter relative to this application and the resulting Official document under Rule 20, or credit any overpayment, to our Account/Order Nos. shown above for which purpose a duplicate copy of this sheet is attached.

This CHARGE STATEMENT does not authorize charge of the issue fee until/unless an issue fee transmittal form is filedPillsbury Winthrop LLP  
Intellectual Property GroupBy Atty: Paul L. SharerReg. No. 36004Sig: Fax: (202) 822-0944Tel: (202) 861-3649

Atty/Sec: PLS/JRH

**NOTE:** File in duplicate with 2 postcard receipts (PAT-103) & attachments.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re National Stage Application of PCT/GB99/02206

ROBERTSON

Group Art Unit: Not Yet Assigned

Appln. No.: Not Yet Assigned

Examiner: Not Yet Assigned

Filed: January 22, 2001

FOR: ACRYLIC POLYMER COMPOSITION

\* \* \* \* \*

January 22, 2001

**PRELIMINARY AMENDMENT**

Hon. Commissioner of Patents  
and Trademarks  
Washington, DC 20231

Sir:

Before beginning examination, kindly amend the above-identified National Stage application, based on the amended claims from the International Preliminary Examination

Report as follows:

**IN THE CLAIMS:**

Please amend the following claims as follows:

Claim 5, line 1, delete "any one of claims 1- 4" and insert -- claim 1--.

Claim 6, line 1, delete "any preceding claim" and insert --claim 1--.

Claim 7, line 1, delete "any preceding claim" and insert --claim 1--.

Claim 10, line 1, delete "any one of claims 1 - 8" and insert --claim 1--.

Please amend claim 9 as follows:

--9. A [a] process for forming an acrylic composition comprising [the steps of]:

(a) mixing together [(i)] 70-99.5% w/w of a polymerisable acrylic monomer or a solution of a polymer in a polymerisable acrylic monomer with [(ii)] 0.5-30% w/w of a dispersion

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comprising 20-50% w/w of a finely divided compound selected from [the] oxides of silicon, titanium, zirconium or aluminum;

- (b) adding to said mixture a quantity of one or more initiator(s) which is sufficient to initiate polymerization of the acrylic monomer under the conditions used; and
- (c) polymerising [causing] the acrylic monomer [to polymerise].--

REMARKS

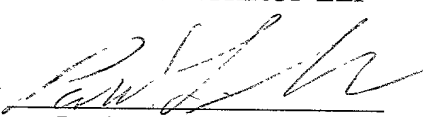
Upon entry of this amendment, there will be no multiple dependent claims in the application. Claim 9 has been amended. It is respectfully submitted that no new matter has been introduced and entry of this Preliminary Amendment is respectfully requested.

It is respectfully submitted that the instant application is in condition for allowance and a Notice to that effect is courteously solicited. If any questions remain, the Examiner is encouraged to call the undersigned attorney to expedite the prosecution of this application.

Respectfully submitted,

PILLSBURY WINTHROP LLP

By

  
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# APPLICATION UNDER UNITED STATES PATENT LAWS

Atty. Dkt. No. PM 276595  
(M#)

Invention: ACRYLIC POLYMER COMPOSITION

Inventor (s): Graeme ROBERTSON  
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This is a:

- ☐ Provisional Application
- ☐ Regular Utility Application
- ☐ Continuing Application  
☒ The contents of the parent are incorporated  
by reference
- ☒ PCT National Phase Application
- ☐ Design Application
- ☐ Reissue Application
- ☐ Plant Application
- ☐ Substitute Specification  
Sub. Spec Filed \_\_\_\_\_  
in App. No. \_\_\_\_\_ / \_\_\_\_\_
- ☐ Marked up Specification re  
Sub. Spec. filed \_\_\_\_\_  
In App. No \_\_\_\_\_ / \_\_\_\_\_

## SPECIFICATION

Acrylic Polymer Composition

The present invention relates to an abrasion resistant polymer composition and a process for its preparation.

Acrylic sheet materials are widely used for building and glazing applications and to form various shaped articles such as baths, sinks, vanity units and shower trays. The abrasion resistance of the acrylic sheet used in such applications is normally required to be as high as possible. One method that is currently used to improve the abrasion resistance of acrylic surfaces involves the application of an abrasion resistant coating to the surface of an acrylic sheet. The coating is typically applied in solution to the acrylic sheet and is then cured, for example by radiation (UV), solvent evaporation or by thermal curing. For example, EP-A-571808 discloses antifogging film, plates and articles comprising an acrylic polymer support and a polymerised and UV reticulated abrasion resistant coating containing acrylic monomers and hydrophilic metal oxide(s). Examples of components within the coating that are thought to provide the abrasion resistant property are titanium, silica, aluminium compounds. Although abrasion-resistant coatings can enhance the performance of acrylic surfaces against abrasion, their use on acrylic sheet which is to be shaped, e.g. by thermoforming, may be limited by the relatively inelastic nature of the coating, which may cause cracking of the coating as the surface is deformed.

Conventional coating technology requires a two step process: polymerising the sheet followed by coating and curing the abrasion resistant formulation. In practice, this often requires a clean room environment to ensure no dust particles become incorporated into the surface layer. There is therefore a significant manufacturing advantage to be gained for an abrasion resistant product which may be delivered in a one-step process.

Curable acrylic compositions containing a high proportion of a mineral filler, such as silica or alumina particles, are well known. These compositions are typically used to form articles such as kitchen sinks or worktops by mixing with a suitable thermal initiator and then pumping them into a heated mould whereupon they are cured to form a solid and inflexible opaque moulded article. These articles generally have a relatively high resistance to abrasion compared to unfilled acrylic sheets of the type which are suitable for thermoforming. The addition of similar fillers at much lower levels to acrylic sheet materials may give some abrasion resistance properties but the polymer formed is hazy

and hence has poor optical properties.

It is therefore an object of the invention to provide an acrylic article which has better resistance to abrasion than unfilled acrylic materials but which has acceptable optical properties for some typical sheet applications.

- 5 Accordingly, in a first aspect, the present invention provides an acrylic composition comprising at least 70% w/w of the residues of at least one polymerisable acrylic monomer, 0.2 - 5% w/w of a finely divided compound comprising at least one oxide selected from silicon, titanium, zirconium and aluminium oxides, and 0.2 - 25% w/w of at least one linking compound which is miscible with said polymerisable acrylic monomer and which is capable of bonding to the surface of the oxide compound.

10 In a second aspect the present invention provides a polymerisable composition comprising at least 70% w/w of at least one polymerisable acrylic monomer, 0.2 - 5% w/w of a finely divided compound comprising at least one oxide selected from silicon, titanium, zirconium and aluminium oxides, and 0.2 - 25% w/w of at least one linking compound which is miscible with said polymerisable acrylic compound and which is capable of bonding to the surface of the oxide compound.

15 In a third aspect the present invention provides a process for forming an acrylic composition comprising the steps of:

(a) mixing together:

- 20 (i) 70 - 99.5 % w/w of a polymerisable acrylic monomer or a solution of a polymer in a polymerisable acrylic monomer with
- (ii) 0.5 - 30% w/w of a dispersion comprising 20 - 50% w/w of a finely divided compound selected from the oxides of silicon, titanium, zirconium or aluminium and 50 - 80% of a linking compound least one linking compound
- 25 which is miscible with said polymerisable acrylic compound and which is capable of bonding to the surface of the oxide compound;
- (b) adding to said mixture a quantity of one or more initiator(s) which is sufficient to initiate polymerisation of the acrylic monomer under the conditions used; and
- (c) causing the acrylic monomer to polymerise.



Although dispersions of colloidal silica particles for example, in e.g. hydroxyethyl methacrylate are known for use in coating compositions used to provide abrasion resistant coatings on acrylic surfaces, it has been surprisingly found that the addition of such a composition containing an abrasion resistant component to the monomer(s) used to make the acrylic polymer before polymerisation results in a polymer with good optical properties and also improved abrasion resistant properties compared to the unmodified polymer.

The polymerisable acrylic monomers are alkyl (alk)acrylic acids and esters thereof, including functionalised monomers such as hydroxy, halogen or amine functionalised acrylate or methacrylate monomers. Preferably the monomer(s) comprise one or more alkyl acrylates, alkyl methacrylates or acrylic or methacrylic acid, e.g. methyl, ethyl, hydroxyethyl, butyl, 2-ethylhexyl, cyclohexyl or phenyl esters of acrylic acid or methacrylic acid. One preferred acrylic material comprises a homopolymer or copolymer of methyl methacrylate comprising 80 - 100% of methyl methacrylate residues and 0 - 20% of an alkyl acrylate or methacrylate selected from those materials listed above.

The at least one linking compound is miscible with the acrylic monomer(s) and preferably contains at least one functional group such as an acrylate or methacrylate group which may be copolymerisable with the acrylic monomers. When more than one functional acrylate or methacrylate group is present, the linking compound may be capable of providing a cross-linking site in the acrylic polymer. The linking compound is also capable of bonding to the surface of the oxide compound and this is conveniently achieved by the use of compounds containing polar groups, e.g. having hydroxyl functionality. Preferred compounds are hydroxyl or other polar group-containing acrylate or methacrylate compounds although other compounds may also be suitable. Suitable compounds include hydroxyethyl methacrylate (HEMA), hexanediol diacrylate, tripropylglycol methacrylate, ethylene glycol monopropylether, 3-aminopropyl trimethoxysilane and ethanolamine or mixtures thereof. Some compounds may perform the function of the linking compound adequately whilst having certain disadvantages in certain applications, e.g. the use of coloured compounds or compounds which develop a colour under the conditions of manufacture of the composition or any article made therefrom may be unsuitable when a clear product is required.

The finely divided oxide compound preferably has an average particle size between 1 and 50 nm, more preferably between 5 and 35 nm. It is present at 0.2 - 5% in the composition, more preferably at 0.5 to 3% by weight. A preferred oxide compound is colloidal silica. The oxide compound is preferably added to the acrylic monomer or polymer/monomer solution in the form of a dispersion in the linking compound. Suitable dispersions are available commercially for use as coating compositions to provide abrasion resistant coatings. Examples of suitable commercial dispersions include the HIGHLINK™ compounds available from Clariant, e.g. Highlink OG 100-30. The ratio of said linking compound to said finely divided oxide is preferably in the range 1:1 - 5:1 (more preferably 2:1 - 4:1) by weight. The dispersion is preferably present at 0.2 to 10%, more preferably 2 to 8% by weight in the polymerisable composition.

The acrylic compositions can be made by conventional free radical, anionic or other polymerisation techniques, for example bulk, solution or suspension with the addition of suitable initiators and optionally chain transfer agents and/or other additives such as cross-linking additives, fillers, pigments, plasticisers, impact modifiers, stabilisers etc. Therefore the monomer(s) are caused to polymerise by initiating the polymerisation reaction, normally by means of activating the added initiator, and maintaining suitable conditions, e.g. an elevated temperature, pressure etc until the required degree of polymerisation has been achieved. Such methods are already very well known to the skilled person and a large number of such methods exist in the art. As one preferred option, free-radical polymerisation is used, e.g. in a bulk polymerisation process used in the well-known cell-casting method of manufacturing high molecular weight acrylic sheets in which a (mixture of) polymerisable monomer(s), optionally with polymer dissolved therein to form a syrup, is mixed with an initiator or mixture of initiators and other additives and filled either into the gap between two glass plates which are separated by a gasket or into a bag or other mould. The polymerisation reaction is then thermally initiated and the polymer allowed to form and cure at elevated temperature. The acrylic composition of the present invention may be in the form of sheets, which may be suitable for shaping by e.g. (thermo)forming, or of powders or pellets, which may be extruded. When a powdered or pelleted compound is required then the method of polymerising the polymer may also be selected from suspension polymerisation, solution polymerisation or by crushing or

pelletising a bulk polymerised product. Methods of forming acrylic polymers by suspension or solution polymerisation are well known in the art and therefore need not be further described.

The present invention is illustrated by reference to the following examples.

5 Example 1 Preparation of cast polymethylmethacrylate (PMMA) sheet

10 A mixture comprising 2,2 - azobisisobutyronitrile (AIBN) (0.08% by weight), HIGHLINK™ OG 100-30 (from Clariant) which is a dispersion of 30% by weight colloidal silica of a particle size 13-30 nm in HEMA (2.5% by weight), with the balance of the composition being made up of a standard PMMA syrup comprising a solution of PMMA in  
15 methylmethacrylate (MMA) monomer was mixed using a high shear mixer at maximum setting for 1 minute. The mixture was placed in a cell comprising two glass sheets spaced 3.2 mm apart from each other by a non metallic gasket. The cell was sealed and immersed in a water bath at 45 °C for 20 hours. The mixture was then post cured for 2 hours at 60 °C followed by 2 hours at 80 °C, followed by heating at a rate of 0.5 °C /min up to 118 °C and held at 118 °C for 1 hour. The cell was then cooled and the glass sheets removed to release the resulting cast PMMA sheet.

20 50 mm square samples of the cast PMMA were abraded by applying to their surface a rotating 33 mm diameter circular abrasive disc comprising aluminium oxide bonded in resin fibres ("ROLOC FINE GREEN" from 3M company) for 60 seconds at a constant 180 rpm under loading forces of 1, 10 and 20 Newtons (N) respectively. The abrasion resistance of each sample was estimated by determining the light transmission and haze before and after the abrasion treatment using a spectrophotometer in accordance with ASTM D1925-76. The results are shown in the table.

Example 2

25 A cast PMMA sheet was made as described in example 1 using only 0.5% w of the Highlink in the formulation. Testing was carried out as before at a loading of 20N.

Example 3 (Comparative) Preparation of coated PMMA samples

A 3 mm thick sample of cast PMMA sheet was coated with a mixture of HIGHLINK OG

100-30 and 0.2% w/w of AIBN initiator at various wet thicknesses of 100, 50, 24 and 12 microns and cured. The resulting coatings were poorly adhered to the substrate and showed evidence of cracking and for this reason they were not tested. In order to improve the coating properties, a coating was formulated from a trifunctional aliphatic polyester urethane acrylate oligomer (Craynor™ 929 from Cray Valley) diluted to 50% w/w in hexanediol diacrylate with the HIGHLINK composition at a ratio of 1:1 by weight. A photoinitiator (Darocur™ 1173) was added at 2% w/w prior to coating. The coating was applied at a wet thickness of 4 microns and cured under UV light in a commercial UV coating apparatus. The coated samples were then tested as described in example 1.

- 10 The results show that the abrasion resistance performance was comparable to that of Examples 1 & 2.

Example 4 (comparative)

50 mm square samples of standard cast PMMA coated at 4 microns wet thickness with UVECRYL™ 29203 (UCB Resins), a UV curable aliphatic urethane acrylate abrasion resistant coating, were prepared and abraded on the coated surface. The optical properties were measured as described in Example 1. The results show that the PMMA of the present invention is at least comparable in abrasion resistance performance to PMMA coated with "UVECRYL 29203".

Example 5 (comparative)

50 mm square samples of unmodified cast PMMA, i.e. PMMA syrup polymerised without the presence of the oxide compound, were abraded and the optical properties measured as described in Example 1. The results show that the abrasion resistance of the samples of the invention are superior to that of the unmodified PMMA, in that the light transmission remains greater and the haze less than that of the unmodified PMMA at all loading levels.

Example 6 (comparative)

A PMMA sample was cast from a similar PMMA in MMA syrup which had been mixed with cristobalite silica (mean particle size 6 nm) dispersed as a slurry in MMA, i.e. so that the linking compound of the invention was not present. The amount of slurry used gave a total concentration of 0.75 %w/w of silica in the total acrylic mixture. The mixture was initiated and polymerised as before. The resulting sample of acrylic polymer was abraded

and tested as described in Example 1. The results show that this material had a much higher haze value than the others and that the light transmission and haze degraded with abrasion.

	Light Transmission				Haze			
Loading (N)	0	1	10	20	0	1	10	20
Ex 1	90.4	88.8	87.3	85.9	1.6	9.7	13.5	16.6
Ex 2	92.3			83.5	0.7			24.5
Ex 3 (comp)	92.1	90.0	89.1	84.2	0.4	6.0	13.0	22.7
Ex 4 (comp)	92.1	88.9	85.9	84.5	0.1	8.5	10.0	27.0
Ex 5 (comp)	92.4	86.7	80.9	82.5	0.2	19.9	34.9	31.6
Ex 6 (comp)	87.0		85.3	81.1	15.7		21.9	36.9

#### Example 7 Thermoforming of samples

PMMA sheet of Examples 1, 3 and 5, was (thermo)formed by placing a mould and sheet assembly in an electric oven preheated at 180 °C for 30 minutes. A two-stage rotary vacuum pump was attached to the mould and maximum vacuum applied. When thermoforming had been completed the assembly was cooled under vacuum until the PMMA surface temperature had dropped to 80 °C or below. The moulded article was then removed from the mould. The resulting mouldings from Examples 1 and 5 were satisfactory in appearance whilst that of Example 3 was shown not to have been fully drawn and cracks were visible on the drawn surface.

## ABSTRACT OF THE DISCLOSURE

An abrasion resistant acrylic composition comprises at least 70% w/w of the residues of at least one polymerisable acrylic monomer, 0.2-5% w/w of a finely divided compound comprising at least one oxide selected from silicon, titanium, zirconium and aluminum oxides, and 0.2-25% w/w of at least one linking compound which is miscible with said polymerisable acrylic monomer and which is capable of bonding to the surface of the oxide compound. The acrylic composition may be thermoformed while retaining its abrasion resistant surface properties.

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12-09-2000

PCT/GB99/02206

CLMS

CLAIMS

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JC02 Rec'd PCT/PTO 22 JAN 2001

- 1 An acrylic composition comprising at least 70% w/w of the residues of at least one polymerisable acrylic monomer, 0.2 - 5% w/w of a finely divided compound comprising at least one oxide selected from silicon, titanium, zirconium and aluminium oxides, and 0.2 - 25% w/w of at least one linking compound which is miscible with said polymerisable acrylic compound and which is capable of bonding to the surface of the oxide compound, wherein the composition excludes a level of polymerisable acrylic monomer of 70% w/w.
- 2 An acrylic composition as claimed in claim 1, wherein the linking compound contains at least one functional group which is copolymerisable with the acrylic monomers and a polar group which is capable of bonding to the surface of the oxide compound.
- 3 An acrylic composition as claimed in claim 2, wherein the linking compound comprises a monofunctional or polyfunctional acrylate or methacrylate compound which additionally contains a polar hydroxyl group.
- 4 An acrylic composition as claimed in claim 3, wherein the linking compound is selected from hydroxyethylmethacrylate, hexanedioldiacrylate or tripropylglycolmethacrylate.
- 5 An acrylic composition as claimed in any one of claims 1 - 4, wherein the finely divided oxide compound comprises colloidal silica.
- 6 An acrylic composition as claimed in any preceding claim, wherein the finely divided oxide compound has an average particle size between 1 and 50 nm.
- 7 An acrylic composition as claimed in any preceding claim, wherein the ratio of said linking compound to said finely divided oxide is preferably in the range 1:1 - 5:1 by weight.
- 8 A polymerisable composition comprising at least 70% w/w of at least one polymerisable acrylic monomer, 0.2 - 5% w/w of a finely divided compound comprising at least one oxide selected from silicon, titanium, zirconium and aluminium oxides, and 0.2 - 25% w/w of at least one linking compound which is miscible with said polymerisable acrylic compound and which is capable of bonding to the surface of the oxide compound, wherein the composition excludes a level of polymerisable acrylic monomer of 70% w/w.
- 9 a process for forming an acrylic composition comprising the steps of:
  - (a) mixing together
    - (i) 70 - 99.5 % w/w of a polymerisable acrylic monomer or a solution of a polymer in a polymerisable acrylic monomer with
    - (ii) 0.5 - 30% w/w of a dispersion comprising 20 - 50% w/w of a finely divided

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compound selected from the oxides of silicon, titanium, zirconium or aluminium  
(b) adding to said mixture a quantity of one or more initiator(s) which is sufficient to initiate polymerisation of the acrylic monomer under the conditions used; and  
(c) causing the acrylic monomer to polymerise.

- 10 An acrylic composition as claimed in any of claims 1 - 8 which is in the form of a sheet, powder, pellet or bead.

FOOTNOTES



FOR UTILITY/DESIGN  
CIP/PCT NATIONAL/PLANT  
ORIGINAL/SUBSTITUTE/SUPPLEMENTAL  
DECLARATIONS

RULE 63 (37 C.F.R. 1.63)  
DECLARATION AND POWER OF ATTORNEY  
FOR PATENT APPLICATION  
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PM & S  
FORM

As a below-named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name, and I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the INVENTION ENTITLED ACRYLIC POLYMER COMPOSITION

the specification of which (CHECK applicable BOX(ES))  
X A. ☐ is attached hereto.  
BOX(ES) → B. ☐ was filed on \_\_\_\_\_ as U.S. Application No. \_\_\_\_\_ /  
→ C. ☒ was filed as PCT International Application No. PCT/ GB99/02206 on July 9, 1999  
and (if applicable to U.S. or PCT application) was amended on \_\_\_\_\_

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56. Except as noted below, I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT International Application which designated at least one other country than the United States, listed below and have also identified below any foreign application for patent or inventor's certificate, or PCT International Application, filed by me or my assignee disclosing the subject matter claimed in this application and having a filing date (1) before that of the application on which priority is claimed, or (2) if no priority claimed, before the filing date of this application

PRIOR FOREIGN APPLICATION(S)

Number	Country	Date first Laid-open or Published	Date Patented or Granted	Priority NOT Claimed
9815730.8	GB	21 July 1998		

If more prior foreign applications, X box at bottom and continue on attached page.

Except as noted below, I hereby claim domestic priority benefit under 35 U.S.C. 119(e) or 120 and/or 365(c) of the indicated United States applications listed below and PCT international applications listed above or below and, if this is a continuation-in-part (CIP) application, insofar as the subject matter disclosed and claimed in this application is in addition to that disclosed in such prior applications, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56 which became available between the filing date of each such prior application and the national or PCT international filing date of this application:

PRIOR U.S. PROVISIONAL, NONPROVISIONAL AND/OR PCT APPLICATION(S)

Application No. (series code/serial no.)	Day/MONTH/Year Filed	Status	Priority NOT Claimed
PCT/GB99/02206	9 July 1999	pending, abandoned, patented pending	

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

And I hereby appoint Pillsbury Winthrop LLP, Intellectual Property Group, 1100 New York Avenue, N.W., Ninth Floor, East Tower, Washington, D.C. 20005-3918, telephone number (202) 861-3000 (to whom all communications are to be directed), and the below-named persons (of the same address) individually and collectively my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith and with the resulting patent, and I hereby authorize them to delete names/numbers below of persons no longer with their firm and to act and rely on instructions from and communicate directly with the person/assignee/attorney/firm/ organization who/which first sends/sent this case to them and by whom/which I hereby declare that I have consented after full disclosure to be represented unless/until I instruct the above firm and/or a below attorney in writing to the contrary

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"X" box ☐ FOR ADDITIONAL INVENTORS, and proceed on the attached page to list each additional inventor.  
☐ See additional foreign priorities on attached page (incorporated herein by reference).

Atty. Dkt. No. PM276595

(M#)